

Fiber Optical Micro-detectors for Oxygen Sensing in Power Plants

Quarterly Technical Report
Reporting Period:
July 1, 2003 to September 30, 2003

Gregory L. Baker*, Ruby N. Ghosh⁺, D.J. Osborn III*

October 2003

DOE Award Number: DE-FC26-02NT41582

*536 Chemistry Building, Department of Chemistry
⁺2167 BPS, Center for Sensor Materials
Michigan State University

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ABSTRACT

Spectroscopy of $\text{Mo}_6\text{Cl}_{12}$ immobilized in a sol-gel matrix and heated to 200 C has been performed. Oxygen quenching of the luminescence was observed. Aging $\text{Mo}_6\text{Cl}_{12}$ to temperatures above 250 °C converts the canary yellow $\text{Mo}_6\text{Cl}_{12}$ to a non-luminescent gray solid. Preliminary experiments point to oxidation of the clusters as the likely cause of thermally induced changes in the physical and optical properties of the clusters.

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INTRODUCTION

Maximizing the efficiency of the combustion process requires real-time control of the correct fuel/oxygen ratio. This requires the ability to sense oxygen levels over a broad range of concentrations with fast response times.

Mussell, Newsham, and Ruud previously reported preliminary studies of the synthesis and optical properties of $\text{Mo}_6\text{Cl}_{12}$ -based clusters relevant to this project. Mussell described the synthesis of the molybdenum clusters, and Newsham gives a good account of the properties of neutral $\text{Mo}_6\text{Cl}_{12}$ clusters and their salts, in both solution and a sol gel matrix. Newsham's data indicate that the photophysical properties of the clusters are maintained in sol gel matrices. To prepare a fiber optic sensor based on $\text{Mo}_6\text{Cl}_{12}$, Ruud dispersed $\text{Mo}_6\text{Cl}_{12}$ in poly[1-trimethylsilyl-1-propyne] (PTMSP), and used a dipping technique to immobilize the composite at the cleaved end of a silica optical fiber. Ghosh and co-workers demonstrated a fast room temperature fiber optic sensor based on oxygen quenching of the luminescence from the PTMSP/ $\text{Mo}_6\text{Cl}_{12}$ composites. While the PTMSP support is adequate for room temperature applications, is unable to withstand the high temperatures associated with combustion in a power plant. To improve the sensor's high temperature performance, we are replacing PTMSP with a thermally stable sol gel matrix that should be able to withstand the higher temperature requirements of the power plant combustion process. The idea of using a sol gel as the support matrix for high temperature oxygen sensor application is not new. Remillard and coworkers have shown that a sol gel supported copper based oxygen sensor can be used in a combustion process. With these facts in hand, we anticipate promising results from our design.

EXECUTIVE SUMMARY

We have accomplished the first step towards the development of an inorganic fiber optic oxygen sensor for high temperature applications, by successfully immobilizing $\text{Mo}_6\text{Cl}_{12}$ in a porous sol-gel film. Quenching of the red luminescence was observed in the Mo-cluster / sol-gel composite films deposited on a quartz substrate following temperature cycling to 200 C. The emission lineshape is unchanged from that of $\text{Mo}_6\text{Cl}_{12}$ in solution, which indicates that the cluster photophysics is not adversely affected by incorporation into the sol-gel matrix or heating to 200 C. The composite film has the mechanical properties required for a harsh environment fiber sensor, as demonstrated by the strong adhesion of the thin films to the quartz substrate. We are currently in the process of characterizing the optical properties of the films *in-situ* at elevated temperatures. These measurements will be performed by heating the sol-gel films using platinum heaters glued to the back of the substrate, with the entire sample immersed in a controlled gas environment.

A preliminary study of the high temperature stability ($>300\text{ }^{\circ}\text{C}$) of the $\text{Mo}_6\text{Cl}_{12}$ clusters in oxygenated environments revealed irreversible changes in the optical absorption spectrum and a loss of the red luminescence that is characteristic of pristine clusters. Thermal aging experiments run in air and under nitrogen point to oxidation of the clusters as the cause of the change in optical properties. We are investigating whether changing the cluster composition will lead to a more stable compound.

EXPERIMENTAL

Preparation of Acetonitrile Complex of $\text{Mo}_6\text{Cl}_{12}$ (Moly Oil)

HPLC grade acetonitrile was used as purchased from Spectrum Chemical Company. In a typical procedure, 75 to 100 mg of $\text{Mo}_6\text{Cl}_{12}$ was placed into a cellulose Soxhlet extraction thimble and extracted with 250 mL of HPLC grade acetonitrile for one week. Some undissolved residue remained in the thimble. The solution was placed in an Erlenmeyer flask and heated to remove solvent until the complex started to precipitate out – indicating maximum concentration. The solution was then removed from heat and the precipitate was allowed to settle. The solution was then filtered through a second Soxhlet extraction thimble into another Erlenmeyer flask. The moly oil solution was then used without further changes.

Sol Gel Preparation

Sol gels were prepared with adjustments made to the water : precursor ratio (R), cosolvent : precursor ratio, sol gel aging time, cosolvent and ethanol evaporation rate, and condensation time in order to optimize film thickness, adhesion, and oxygen permeability. As previously shown by MacCraith and coworkers [1,2,3], these parameters have a large effect on sol gel films. As previously shown [3], the aging time did seem to have the largest effect. The key to forming good films seemed to be the viscosity of the sol gel solution, and the easiest way to monitor it initially was by adjusting the aging time and the condensation time after aging and prior to dip coating. Adjustment of the condensation time after aging was where our greatest advances were made. By dipping slides at different times after aging, a film was finally achieved that gave reasonable quenching results. The adhesive and film thickness properties were monitored qualitatively.

In a typical experiment, moly oil (1.4 mL, 5×10^{-4} M) was added to tetraethyl orthosilicate (TEOS) (2.0 mL, 9 mmol) in an Erlenmeyer flask. Water (0.65 mL, pH = 1 using HCl) was added to the flask and the solution was stirred for 1 hour at room temperature. After stirring, the solution was transferred to a hot oil bath at 70 °C for a period of time (aging). After aging, the solution was transferred to a 20 mL vial and capped for later dip coating.

Preparation of $\text{Mo}_6\text{Cl}_{12}$ / sol-gel composite films

Thin films of $\text{Mo}_6\text{Cl}_{12}$ / sol-gel composite were deposited on quartz slides using four different techniques to determine the parameters most suitable for good adhesion. The first method involved simply rinsing with water and then methanol and gave very poor results. The second method involved cleaning the slides using a previously described process [1]. The slides were rinsed with distilled water, methanol and acetone, conditioned in distilled water at 70 °C for 24 hours, and stored under distilled water until use. The third method involved washing with Alconox, rinsing with distilled water, soaking in a 1:1 mixture of concentrated sulfuric acid and 30% hydrogen peroxide, followed by rinsing with distilled water for at least 1 hour, and storing in distilled water until use. In the fourth method, the slides were washed with Alconox, rinsed with distilled water, soaked in a base bath, rinsed with distilled water for at least 1 hour, and stored in distilled water until use. Just prior to use, the slides were removed from distilled

water and dried by blowing them off with nitrogen gas. The slides were handled with gloves and tweezers in order to minimize surface contamination. The fourth method was chosen, because it gave the best results for sol gel adhesion.

Dip Coating - Quartz or glass slides were then dipped by hand at a rate of approximately 1 mm/sec. The slides were then placed directly onto a piece of aluminum foil or into a vial and capped. Different number of coatings and times between coats were attempted. The sol gel solution was capped after each dip coat in order to minimize the rate of formation of the gel. The mechanical and optical properties of two samples, slides 15F and 15G, are described in the text related to Figures 8, 9 and 10. Slide 15F was prepared using a three dip coat process with the first coat 64 hours and 30 minutes, second coat 64 hours and 40 minutes, and the third coat 65 hours and 7 minutes after removal of the sol gel solution from the hot oil bath at 70 °C. The slide was cured at room temperature in a capped vial for 320 hours and 2 minutes before placing in the oven at 70 °C. It was then heated in the oven for 24 hours and 19 minutes. Slide 15J was prepared using a two dip coat process with the first coat 312 hours and 12 minutes and second coat 312 hours and 22 minutes after removal of the sol gel solution from the hot oil bath at 70 °C. The slide was cured at room temperature in a capped vial for 94 hours and 45 minutes before placing in the oven at 70 °C. It was then heated in the oven for 23 hours and 30 minutes.

Fluorescence

The fluorescence measurements were performed using a Fluorolog-3 instrument from Instruments S.A., Inc. The system includes a single Czerny-Turner excitation spectrometer with a 1200g/mm ruled grating blazed at 330nm and a single Czerny-Turner emission spectrometer with a 1200g/mm holographic grating blazed at 630 nm. The excitation optics consists of a 450W ozone free Xe lamp, followed by a 270-380 nm bandpass filter (Oriel 1124). A Si photodiode is used to continuously monitor the lamp signal. The detection optics consists of 603.2 nm long wave pass filter (CVI) followed by a multi-alkali photo multiplier tube (Hamamatsu R928) with photon counting electronics. Data processing was performed using the Datamax (version 2.2) software package supplied with the instrument. Spectra were obtained by exciting at 313 nm with a 5 nm slit and scanning the emission monochromatic from 500 to 850 nm with a 1 nm slit.

Two types of spectra are presented. The “uncorrected spectra” are the raw data from the photo multiplier tube, without correcting for the spectral response function of either the PMT or emission grating. Therefore the “uncorrected spectra” do not show the true emission lineshape. The “corrected spectra” includes corrections for the spectral response of the PMT and emission grating, and represents the true emission lineshape. The “uncorrected spectra” will show a peak in the 670 - 680 nm range, and a constant background offset of 500 - 1000 cps, due to the PMT dark count. The “corrected spectra” have a broad peak in the 720 - 760 nm range, without any background offset.

Measurements of the cluster fluorescence in solution with different concentrations of dissolved oxygen were performed by placing the solution in a quartz cuvette sealed with an airtight septum. The atmosphere measurements (~20% oxygen) were performed first. The measurements in nitrogen gas were performed by sealing the quartz cuvette with an

airtight septum, then bubbling 99.999% purity nitrogen gas through the solution for 10 minutes.

Measurements of the sol-gel immobilized clusters in different oxygen environments were made in the same setup. The sol-gel films were deposited on rectangular (14 mm x 20 mm), 2mm thick quartz slides. The slides are designed to fit along the diagonal of the 1 cm x 1 cm of the square quartz cuvette. The slides were purged *in-situ* and care was taken to not move the excitation spot between the atmospheric and <0.001% oxygen measurements. This allows us to measure the degree of oxygen quenching in the films to +/- 20%, despite the observed inhomogeneities in film thickness.

Optical Microscopy of Thin Films

Polarized optical microscopy images were acquired using a Nikon Optiphot2-Pol equipped with a Sony Hyper HAD CCD-IRIS/RGB color video camera (model DXC-151A). The camera was connected to a PC using a Sony camera adapter (model CMA-D2). The images were viewed using a Sony Trinitron color video monitor. Images were taken using Hauppauge computer works Win/TV software (version 2.4.17052). Images collected at 0 and 90° to characterize the birefringence of the samples and a qualitative measure of their degree of crystallinity. A programmable hot stage (Mettler FP82) was used to collect images at elevated temperatures.

Thermal Analysis

Thermogravimetric analyses were performed using a Perkin-Elmer TGA-7. $\text{Mo}_6\text{Cl}_{12}$ samples were typically measured in either in air or under nitrogen at a heating rate of 10°C/min. Any deviations from this protocol are described in the figure captions.

Microwelding for construction of the Pt heater assembly

We have placed an order for a parallel gap resistance micro-joiner, a Unibond II system from Unitek Equipment. The system will be used to make electrical contacts for the Pt heater assembly. Our system is scheduled for delivery and installation in the middle of November. We were previously using a instrument at our colleague's facility at Ford.

RESULTS AND DISCUSSION

Characterization of $\text{Mo}_6\text{Cl}_{12}$ at $T > 200^\circ\text{C}$

$\text{Mo}_6\text{Cl}_{12}$ crystallizes from aqueous HCl as canary yellow needles. From earlier microscopy studies, we observed that the color of the clusters is temperature dependent, evolving from its characteristics yellow to crimson red and eventually gray. The chromatic changes are reversible up to 250° , and the room temperature photophysics of the clusters cycled to 250° are unchanged. Thermogravimetric analyses (TGA) of $\text{Mo}_6\text{Cl}_{12}$ run in air show a gradual loss of weight during heating to 200°C at $10^\circ/\text{min}$ (**Figure 1**). As shown in **Figure 2**, the clusters stack in columns with water bridging the columns, and these water molecules are reversibly lost from the structure on heating. Irreversible effects were seen for $\text{Mo}_6\text{Cl}_{12}$ samples heated to 300°C at $10^\circ/\text{min}$. As shown in **Figure 3**, $\text{Mo}_6\text{Cl}_{12}$ changes from yellow to gray, and the gray color persists after cooling the clusters to room temperature. The absorption spectrum of $\text{Mo}_6\text{Cl}_{12}$ shows two prominent shoulders at 313 and 340 nm. Samples heated at $10^\circ/\text{min}$ to as high as 250° show only minor changes in their absorption and emission spectra after cooling to room temperature (**Figures 4 and 5**). These measurements were made using 4 mg of heated sample dissolved in 6 M HCl. However, the 313 and 340 nm features in the absorption spectrum are rapidly lost in samples heated to 300° , and more importantly, the characteristic red luminescence of $\text{Mo}_6\text{Cl}_{12}$ is absent in the gray material.

The TGA data show a second weight loss event beginning at $T > 250^\circ$, and while the exact nature of the structural change is not yet certain, the enhanced temperature stability of the clusters in nitrogen (**Figure 6**) suggest the formation of a molybdenum oxide. Samples of the gray material have been submitted for chemical analysis. Solubility tests confirm a structural change; unlike $\text{Mo}_6\text{Cl}_{12}$, the gray material is insoluble in methanol. Interestingly, HCl will convert moderately degraded $\text{Mo}_6\text{Cl}_{12}$ (green, an intermediate shade) to its initial yellow. Unfortunately, formation of a yellow product was not accompanied by restoration of the red luminescence characteristic of $\text{Mo}_6\text{Cl}_{12}$.

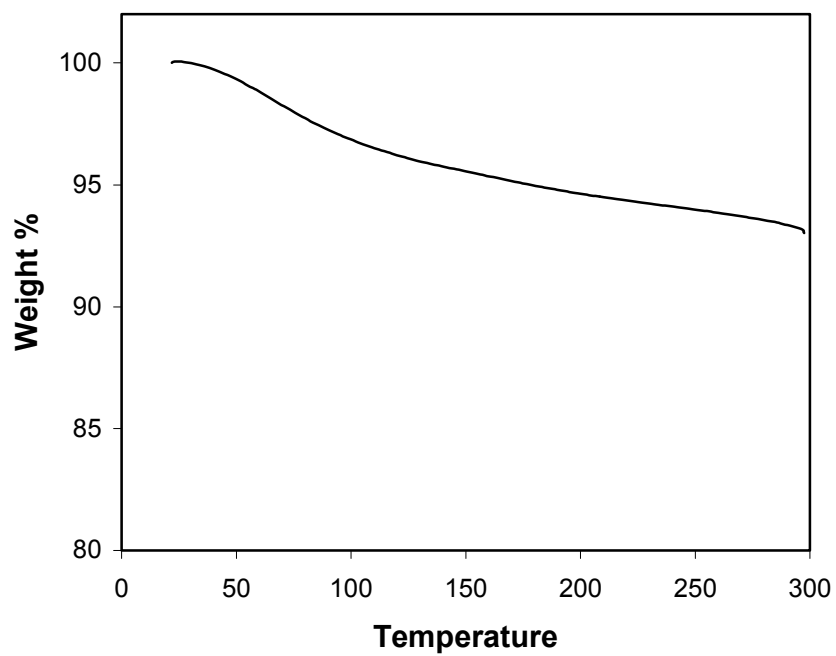


Figure 1. TGA analysis of $\text{Mo}_6\text{Cl}_{12}$ in air. Heating rate: $10^\circ\text{C}/\text{min}$.

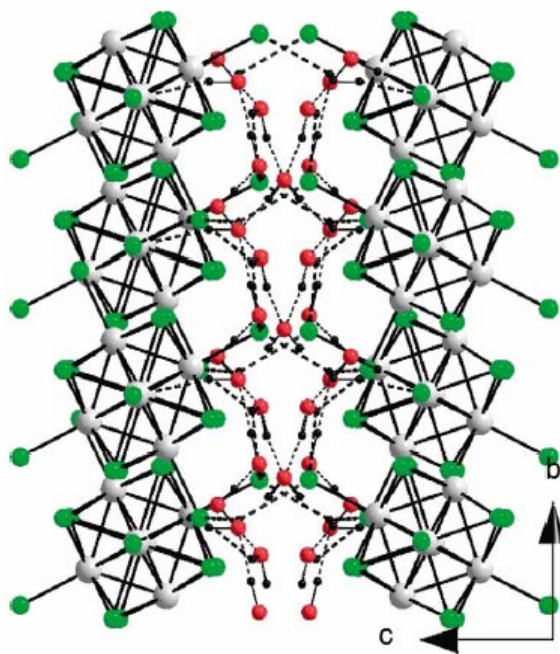


Figure 2. The structure of $\text{Mo}_6\text{Cl}_{12}$ (from reference 4) showing the columns of clusters bridged by water molecules.



Figure 3. Left: Pristine needles of $\text{Mo}_6\text{Cl}_{12}$, Right: Gray needles formed by ageing at 300°C for one hour.

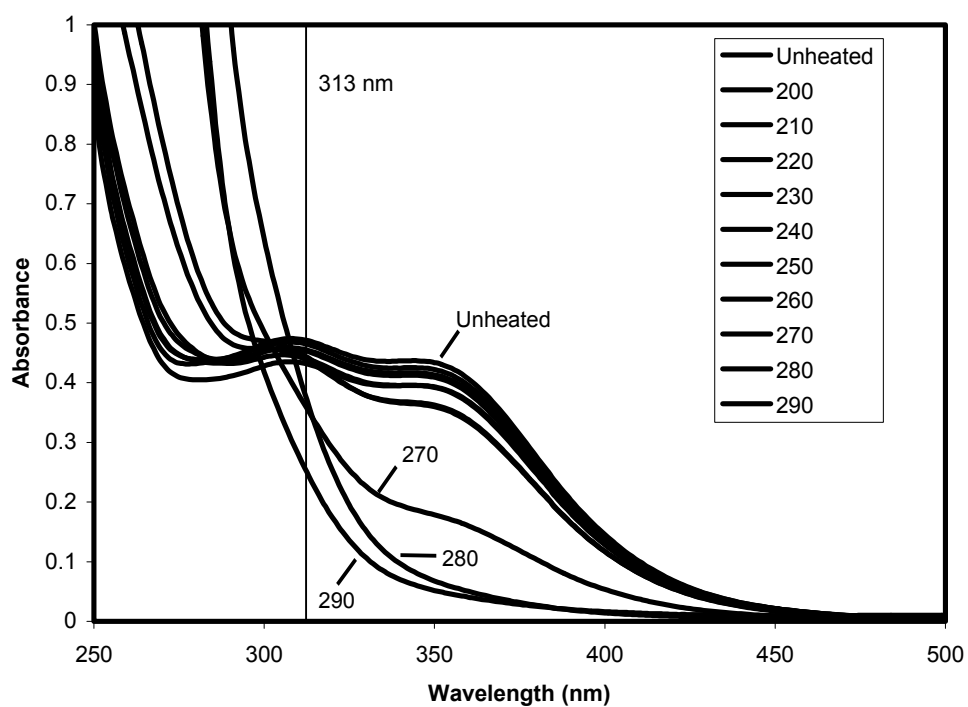


Figure 4. Absorption spectra of $\text{Mo}_6\text{Cl}_{12}$ clusters in 6 M HCl (concentration = 4g/L). Heating protocol: heat to to the indicated temperatures at $10^\circ/\text{min}$, hold at that temperature for one hour, and cool to room temperature.

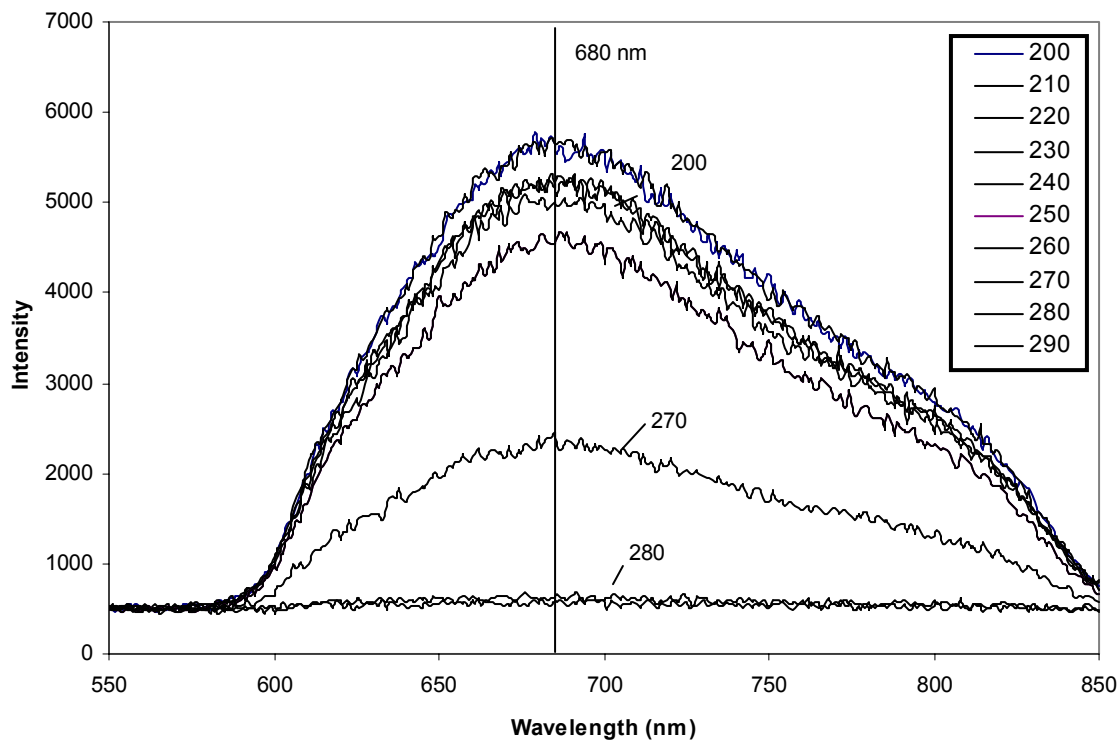


Figure 5. Uncorrected luminescence spectra of $\text{Mo}_6\text{Cl}_{12}$ after heating at $10\text{ }^\circ\text{C/min}$ to the indicated temperature and held for 1 hour. The cluster were heated to the indicated temperature, then dissolved in 6M HCl prior to the emission measurements. The excitation wavelength was 313 nm.

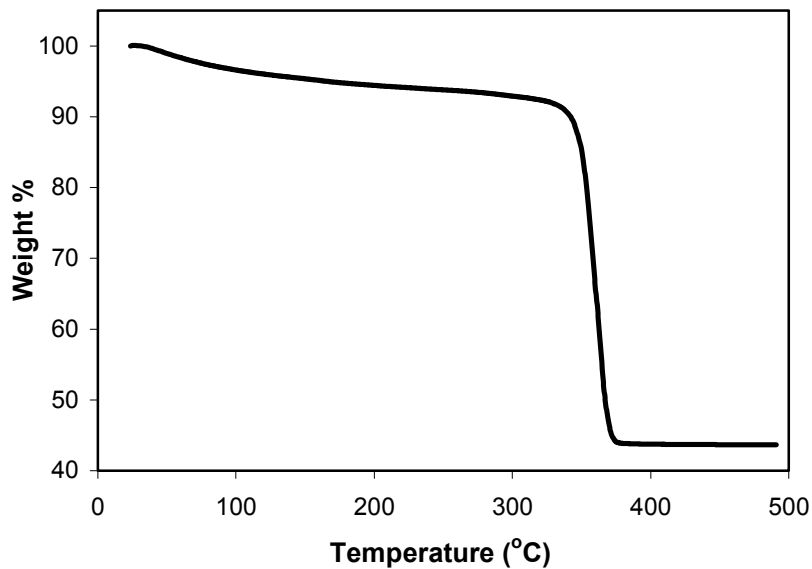


Figure 6. TGA analysis of $\text{Mo}_6\text{Cl}_{12}$ in nitrogen. Heating rate: $10\text{ }^\circ\text{C/min}$.

Optical characterization of the Acetonitrile Complex of $\text{Mo}_6\text{Cl}_{12}$ (Moly Oil)

Because of its high solubility in nonpolar to moderately polar solvents, the acetonitrile complex of $\text{Mo}_6\text{Cl}_{12}$ (Moly oil) is well-suited for sol-gel syntheses that lead to the Mo -clusters immobilized in an oxygen permeable matrix. Measurements of the oxygen quenching properties of the Moly oil were used as a quality control for Moly oil produced by the sohxlet extraction technique. **Figure 7** shows absorbance and emission spectra of a 5×10^{-3} mole/L solution of Moly oil in acetonitrile. to obtain an absorbance of ~ 0.1 at an excitation wavelength of 313 nm. As shown in the figure, ratio of luminescence in and pure nitrogen ($<0.001\%$ oxygen) and air (20% oxygen) is ~ 12 . We previously determined that 12X quenching at an absorbance of ~ 0.1 corresponds to primarily a solution of isolated single $\text{Mo}_6\text{Cl}_{12}$ clusters, conditions that resulting in the maximum degree of luminescence quenching by oxygen.

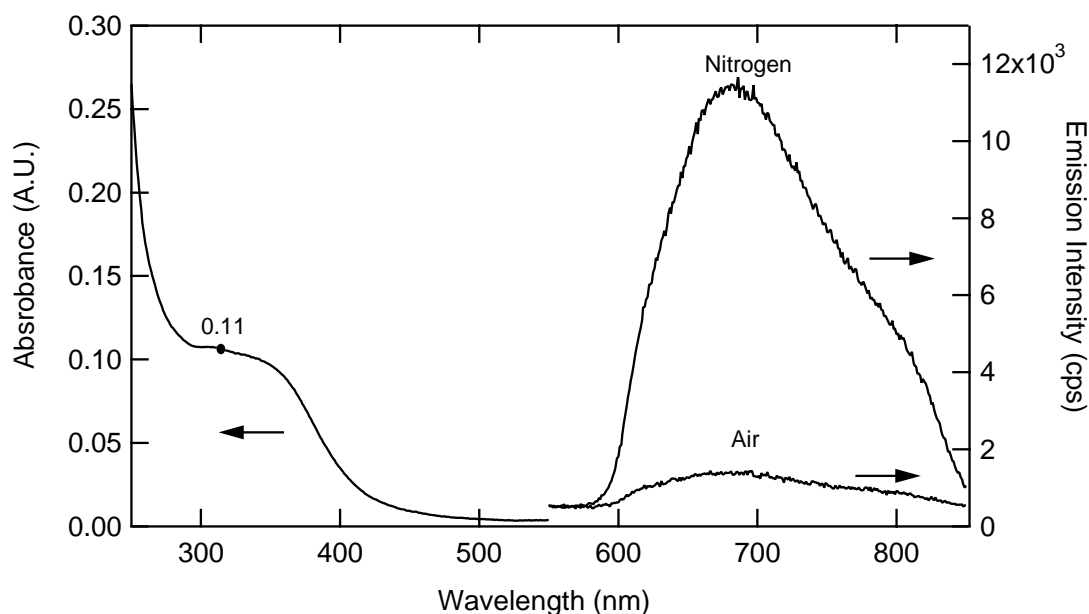


Figure 7. Absorbance and emission spectra of Moly oil in acetonitrile ($\sim 5 \times 10^{-4}$ mol / L). The emission spectra is the “uncorrected” raw data, taken with an excitation wavelength of 313 nm. Quenching of $\sim 12\text{X}$ is observed between nitrogen ($<0.001\%$ oxygen) and air ($\sim 20\%$ oxygen).

Oxygen quenching of Mo-cluster/sol-gel composite films following heat cycling

Thin films of the Mo-cluster/sol-gel composite, produced from the Moly oil (shown in Fig. 7), were deposited on quartz slides and heated to 200 °C for 1 hour. Shown in **Figure 8**, are optical micrographs of two of the films, slide 15F and 15J. The thickness and porosity of the films are a function of how long the sol-gel has aged prior to dip coating. The film on slide 15F was deposited in three coatings at approximately 65 hours, whereas for slide 15J two coatings were applied at approximately 312 hours.

Slide 15F, which is thinner than 15J, shows a fine network of cracks that remain essentially unchanged after heating. This film adheres well to the quartz substrate (even after heat cycling), attempts to scratch the film to measure thickness using a surface profilometer were not successful. The domain size is on the order of 100 microns. Since the core diameter of the optical fiber we will be using is on the order of 100 microns, this process this process is expected to produce crack free Mo-cluster/sol-gel composite films that will completely coat the fiber end. On the other hand, some of the domains on slide 15J, which is thicker than 15F, delaminated upon heating to 200 °C. In addition the domains appear to not be connected, with voids free of the Mo-cluster composite film. Although, a slightly higher degree of oxygen quenching was observed in this film, the mechanical properties are inferior to that of 15F

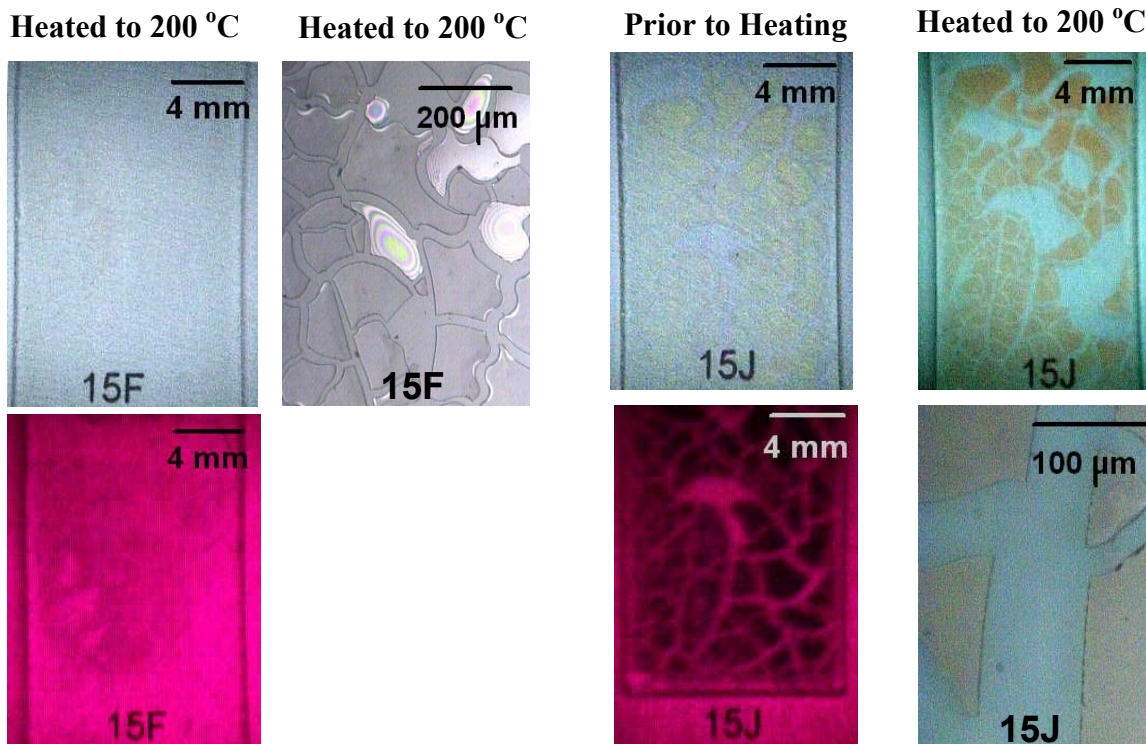


Figure 8. Optical micrographs of $\text{Mo}_6\text{Cl}_{12}$ clusters immobilized in a sol-gel matrix. Shown are two composite films, 15F and 15J, deposited on quartz slides. Slide 15 F is shown after heating to 200 °C and 15J before and after 200 °C. The red micrographs are of the same area as the image immediately above, but color enhanced to better visualize the film cracking.

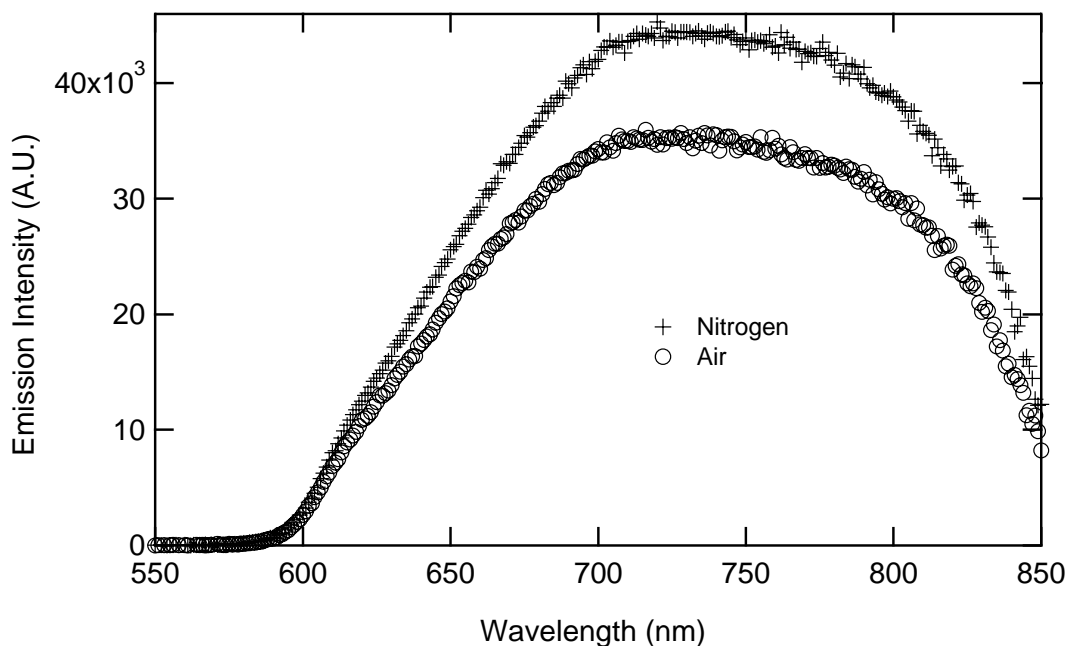


Figure 9. Emission spectra of Mo-cluster / sol-gel composite film 15F, prior to heat treatment. Quenching of $\sim 1.3X$ is observed between nitrogen ($<0.001\%$ oxygen) and air ($\sim 20\%$ oxygen). Excitation wavelength is 313 nm.

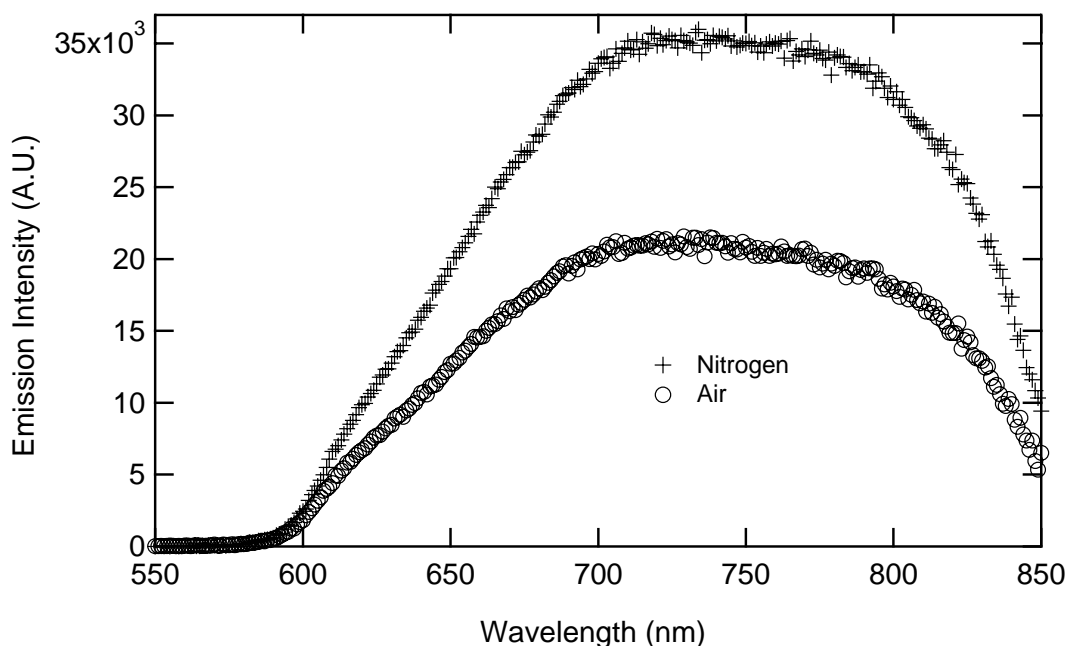


Figure 10. Emission spectra of Mo-cluster / sol-gel composite film 15F, after heating to 200 C for one hour. Quenching of $\sim 1.7X$ is observed between nitrogen ($<0.001\%$ oxygen) and air ($\sim 20\%$ oxygen). Excitation wavelength is 313 nm.

The emission spectra of the Mo-cluster / sol-gel film 15F prior to heating is shown in **Figure 9** and after heating to 200 C for one hour in **Figure 10**. Oxygen quenching of the luminescence is observed in both cases. The difference in degree of quenching and absolute magnitude of the signal are due to the spatial inhomogeneities in the film, as shown in **Figure 8**. Since the excitation spot size is about 2 mm x 10 mm, we are averaging over a large number of the 100 micron domains. In addition, care was taken during the measurements to keep the excitation spot stable during gas exchange. Note that the clusters immobilized in the sol-gel matrix after heat treatment have the same emission lineshape as the isolated clusters in solution (**Figure7**). This indicates that neither the sol-gel chemistry nor heating to 200 C have any adverse effects on the cluster photophysics. We believe that the lower degree of oxygen quenching in the sol-gel matrix as compared to the solution results is due to the porosity of the sol-gel matrix. We are in the process of modifying the sol-gel porosity by adjusting the aging time of the gel.

CONCLUSIONS

The first step towards development of an inorganic fiber optic oxygen sensor for high temperature applications has been accomplished by successfully immobilizing Mo₆Cl₁₂ in a porous sol-gel film and measuring the oxygen quenching of the red luminescence from films that were temperature cycling to 200 °C. Experiments are currently in progress to characterize the optical properties of the films *in-situ* at elevated temperatures.

Parallel thermogravimetric analysis and optical microscopy studies show that at >250 °C in air, the optical properties of Mo₆Cl₁₂ clusters irreversibly degrade and yield a gray, non-luminescent solid. Initial data suggest oxidation of the cluster, a conclusion that will be confirmed by chemical analysis. We are investigating whether changes in the cluster composition, will lead to more stable luminescent compounds.

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None.

LIST OF ACRONYMS AND ABBREVIATIONS

HCl – Hydrochloric Acid

MeOH – Methanol

CH₃CN – Acetonitrile